SELECTIVE OXIDATION OF METHANE TO FORMALDEHYDE OVER VARIOUS CATALYSTS

By

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INTRODUCTION

The conversion of methane into useful intermediate oxidation products instead of complete oxidation to $CO_2$ or partial oxidation to CO is one of the most challenging problems for catalysis research (1). Oxidative coupling leading to the formation of ethane and ethylene from methane (2), (3), (4) and production of oxygenates as methanol and formaldehyde (5), (6), (7), (8) are the two main directions pursued so far and several promising systems have emerged although with low yields. The ultimate goal is to obtain useful intermediates as higher hydrocarbons and/or oxygenates from the main source of methane, the natural gas.

RESULTS AND DISCUSSION

Activity of Vycor- Quartz reactor tubes

Vycor glass has proven to be active in the n-butene isomerization at room temperature (9) as well as in the adsorption of ammonia at 150 °C (10). It was generally believed that the surface hydroxyl groups played an important role in the adsorption, being capable of forming hydrogen bonds with the adsorbates. Sheppard and Yates studied the interaction of various molecules with Vycor glass by infrared spectroscopy (11). In the case of methane a new band, not present in the gas phase spectrum appeared, and it was attributed to physical adsorption. Similar infrared spectroscopy results were obtained in a study of the adsorption of methane on ZSM-5 zeolites by Yamazaki et al (12). Cheaney and Walsh (13) observed a high activity of Vycor glass tubes in the combustion of methane. They attributed the activity to the deposition of a silicic acid layer on the glass

surface during the manufacture of the Vycor glass which included a treatment with HF. When silica tubes were coated with silicic acid, the high $CH_4$ combustion activity of the Vycor tubes could be reproduced (13).

Throughout the course of our work a small amount of ethane , from 0.14 mol % to 1.25 mol % based on methane was present in the feed stream. Table 1 summarizes the total conversion of methane and the selectivities of the various products obtained in our work over quartz and Vycor glass tubes. At a $CH_4/O_2$ molar ratio of about 1 and over the temperature range of 893 to 993 K both tube surfaces produced $C_2H_4$ , $C_2H_6$ , HCHO and $CO_2$. The formaldehyde was identified by Gas Chromatography and Mass Spectrometry. Under the reaction conditions used here, CO was observed only over Vycor glass at temperatures > 940 K. The CO production occurred mainly at the expense of HCHO. At a given temperature, the total methane conversion, over Vycor glass was much higher than the one over quartz. At similar conversions (0.41% at 928 K for Vycor glass and 0.37% at 993 K for quartz ) the $CO_2$ selectivity over Vycor glass was much lower than the one observed over quartz whereas the HCHO selectivity was somewhat higher. The very substantial differences in activity and selectivity between Vycor and quartz reactors despite identical flow conditions and reactor geometries imply that gas interactions sensitive to the nature of the tube surfaces occur. However , in view of the high temperatures, a contribution of gas phase reactions cannot be ruled out.

The residence time has a very significant effect on the product distribution. Fig. 1 illustrates this effect for a quartz reactor at 993 K where the residence time was increased from 3.3 s to 13.2 s by reducing the flowrates by a factor of four while keeping the $CH_4 / O_2$ ratio close to 1. The total methane conversion increased from 0.3% to 2.52% . At a residence time of 3.3 s the formaldehyde selectivity was 60% and the combined $C_2H_4$ and $C_2H_6$ selectivity was 27%. The remaining 13% consisted of $CO_2$. The short residence time quartz runs did not produce any CO. At the long residence time run of 13.2 s CO was generated at the expense primarily of HCHO. This implies that long residence times increase the probability of CO formation via the decomposition of HCHO, a reaction sequence analogous to that observed in the combustion of methane (14) . Similar residence time effects were observed in the Vycor reactors.

The methane to oxygen ratio is another important factor influencing the product distribution. Oxygen rich mixtures strongly favor the overall rate of methane reaction and the rate of CO formation (at the expense of formaldehyde). In view of the blank activity of the quartz, an upper temperature limit of 893 K was imposed on runs with catalyst powders placed into quartz reactors.

Activity of silica based compounds

Various silica based compounds in powder form, including silicic acid, Cab-O-Sil, and Ludox gel exhibited similar trends of methane conversion as the empty Vycor and quartz reactors, although at much lower temperatures. Methane to oxygen ratios lower than one enhanced the activity of these catalysts, in accordance with the behavior observed in the Vycor brand and quartz tubes. Short residence times favored the selectivity of HCHO .

Table 2 compares the overall rate of methane reaction and the selectivity over the various silica compounds for a $CH_4 /O_2$ ratio of close to 1 at a temperature of 893 K. The rate of reaction is reported in two different ways, based on the weight and the surface area of the catalysts as determined after the reaction.

TABLE 1

Conversion and selectivity achieved over Vycor and quartz U tubes at $CH_4 / O_2$ =1.14

| | T(K) | % total methane conversion | $C_2H_4$ | $C_2H_6$ | HCHO | CO | $CO_2$ |
|---|---|---|---|---|---|---|---|
| | | | | **% Selectivity** | | | |
| Vycor | 893 | 0.26 | 2 | 15 | 81 | - | 2 |
| | 913 | 0.31 | 3 | 13 | 81 | - | 3 |
| | 928 | 0.41 | 4 | 17 | 76 | - | 3 |
| | 943 | 0.95 | 4 | 12 | 44 | 35 | 5 |
| | 958 | 1.44 | 4 | 15 | 40 | 37 | 4 |
| | 973 | 2.26 | 5 | 17 | 34 | 41 | 3 |
| | 993 | 3.93 | 7 | 19 | 27 | 45 | 2 |
| quartz | 963 | 0.13 | 8 | 13 | 62 | - | 17 |
| | 993 | 0.37 | 9 | 18 | 60 | - | 13 |

Flowrates : 10% $CH_4$ in Ar=29.7 $cm^3$ STP /min, $O_2$=2.6 $cm^3$ STP/min. P= 205 kPa
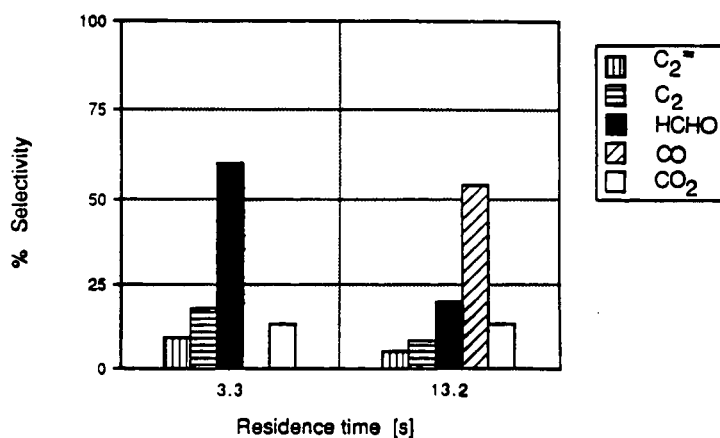


FIGURE 1  $CH_4$ oxidation over empty quartz reactors. Effect of the residence time on the product distribution at 993 K and $CH_4 / O_2$ close to 1

TABLE 2

Activity and selectivity of various silica compounds at 893 K and $CH_4 / O_2$ close to 1

| Compound | Pressure [kPa] | Overall $CH_4$ reaction rate [mol/g s] | Overall $CH_4$ reaction rate [mol/$m^2$ s] | Surface area after reaction [$m^2$/g] | % Selectivity | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $C_2H_4$ | HCHO | CO | $CO_2$ |
| Silicic acid | 218[a] | 1.98 E-7[c] | 0.72 E-9 | 274 | 1 | 23 | 66 | 10 |
| | 340[b] | 2.6 E-7 | 0.95 E-9 | 274 | 7 | 47 | 37 | 9 |
| | 515[b] | 4.2 E-7 | 1.53 E-9 | 274 | 1 | 26 | 63 | 11 |
| Cab-O-Sil | 308[b] | 2.75 E-7 | 1.44 E-9 | 191 | 1 | 30 | 44 | 24 |
| Ludox gel | 377[b] | 0.9 E-7 | 0.87 E-9 | 105 | 1 | 27 | 67 | 5 |

[a] Flowrates: 10% $CH_4$ in Ar=29.7 $cm^3$ STP / min, $O_2$=2.6 $cm^3$ STP / min.  [b] Flowrates: 10% $CH_4$ in Ar= 46.8 $cm^3$ STP / min, $O_2$=5.2 $cm^3$ STP / min.  [c] 1.98E-7 corresponds to $1.98 \times 10^{-7}$

All three catalysts produced $C_2H_4$, HCHO, CO and $CO_2$. From the silicic acid runs, a trend emerged of increasing rate of methane reaction with increasing pressure. On a weight basis, silicic acid and Cab-O-Sil were more active than Ludox gel. When normalized on a surface area basis the differences in reaction rates became less pronounced. Therefore, it is very likely that the high per weight activities of silicic acid and Cab-O-Sil can be attributed to their high surface areas . A similar surface area effect could also explain the relatively high blank activity of empty Vycor glass reactors compared to the quartz reactors. Vycor glass is much more porous than quartz, and consequently, Vycor has a higher surface area.

Figure 2 shows the Arrhenius plots for the overall rate of $CH_4$ reaction as well as for the rates of formation of $C_2H_4$, HCHO, CO and $CO_2$ over silicic acid at a pressure of 585 kPa . The temperatures were randomly selected within the range of 783 - 893 K . Very good linear fit of the Arrhenius plots was achieved excluding the possibility of substantial catalyst deactivation from one run to the next. In the case of formaldehyde, however , at temperatures higher than 853 K a deviation from linearity was observed in the Arrhenius plot, probably due to secondary reactions of formaldehyde to CO and $CO_2$. The apparent activation energies for the overall rate of methane reaction and the formation of the various products are summarized in Table 3. For comparison, the apparent activation energy values for methane oxidation in empty Vycor glass tubes were also determined . The 95% confidence intervals used to estimate the activation energy error margin are also given in Table 3.

The apparent activation energies over silicic acid were generally lower than those over Vycor glass. On both silicic acid and Vycor glass , the apparent activation energy values for formaldehyde were very low and had within experimental error the same value.
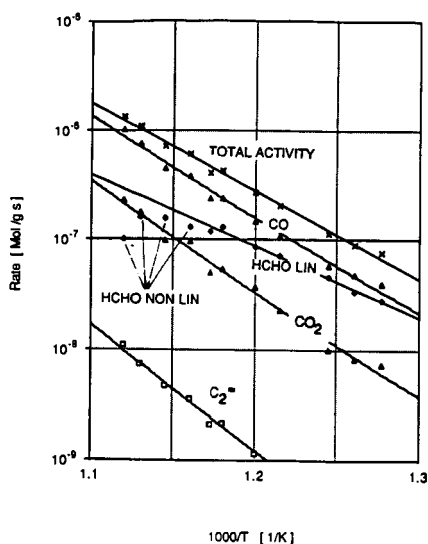
FIGURE 2 Arrhenius plots for silicic acid at 585 kPa and 783-893 K. Flowrates : 10% $CH_4$ in Ar=39.8 $cm^3$ STP / min, $O_2$=4 $cm^3$ STP / min . The plot for HCHO is divided into a linear (HCHO LIN) and non linear portion (HCHO NON LIN)
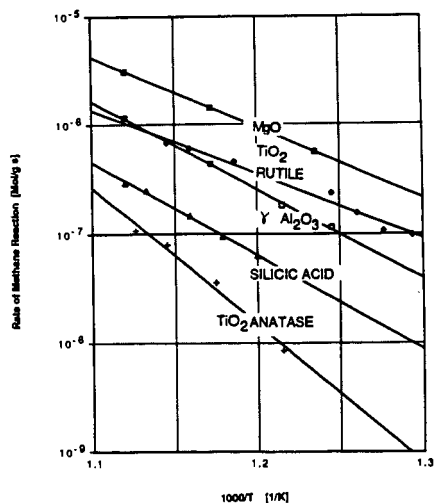


FIGURE 3 Arrhenius plots for the methane reaction rates over MgO (P=205 kPa, $CH_4/O_2$=1), Gamma $Al_2O_3$ (P=294 kPa, $CH_4 / O_2$=0.1), Silicic acid (P=380 kPa, $CH_4/O_2$=1), $TiO_2$ rutile (P=515 kPa, $CH_4/O_2$=1) and $TiO_2$ anatase (P=510 kPa, $CH_4/O_2$=1)

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TABLE 3

Apparent activation energies for the rate of methane reaction and rates of product formation over silicic acid (at 585 kPa, 783-893 K) and Vycor glass (at 205 kPa, 893-993 K).

|  | Silicic acid<br>[ kJ/mol ] | Vycor glass<br>[ kJ/mol ] |
|---|---|---|
| Overall $CH_4$ Reaction | 154 ±10 | 217 ± 49 |
| $C_2H_4$ | 213 ±18 | 299± 39 |
| $C_2H_6$ | (not formed) | 236 ±59 |
| HCHO | 125 ±15 ( linear portion of plot) | 123 ±19 |
| CO | 171 ± 15 | 264 ± 34 |
| $CO_2$ | 184 ±18 | ( non linear) |

This might imply that once the methane molecule is activated the formation of formaldehyde is not dependent on the nature of the catalytic surface and probably occurs in the gas phase. The difference in the activation energy for CO , however, suggests that the subsequent oxidation and/or decomposition of formaldehyde is sensitive to the nature of the catalytic surface or reactor walls.

The deactivation characteristics of silicic acid were also studied by monitoring its activity over a long time period. The methane oxidation activity maintenance was excellent over a period of 16 hrs at 863 K.

Effect of catalyst acidity

In order to investigate the effect of catalyst acidity on methane oxidation, MgO, gamma $Al_2O_3$ as well as two forms of $TiO_2$ , rutile and anatase, were selected for a comparison with silicic acid. Figure 3 shows the rates of the overall methane reaction over these materials in the form of Arrhenius plots. The basic MgO was the most active catalyst. The rates over gamma alumina and rutile were of the same order of magnitude. The lowest rates were obtained over the anatase. Under our reaction conditions, only the moderately acidic silicic acid and the anatase produced formaldehyde. The formaldehyde yields over the anatase, however, were much lower than the ones over the silicic acid. Gamma $Al_2O_3$ and MgO do not seem to preserve formaldehyde, yielding instead deep oxidation products CO and $CO_2$. Rutile drives the reaction to complete oxidation, producing almost exclusively $CO_2$ . The very substantial difference between the activity the rutile and anatase $TiO_2$ forms could be attributed to different oxygen adsorption characteristics, possibly induced by the open structure of the rutile (15).

In the case of the gamma $Al_2O_3$ and MgO , the $CO_2$ selectivity increased with temperature at the expense of CO, whereas for silicic acid the $CO_2$ selectivity remained almost unchanged at 10 to 13 %. As a consequence,

silicic acid appears to be very promising for the conversion of methane into products besides $CO_2$, because it suppresses the $CO_2$ production at higher temperatures and higher conversions

### Effect of small amounts of ethane on the selective methane oxidation over silicic acid and quartz glass

Gesser et al [16] as well as Foster [17] in their reviews of early work on the oxidation of methane to methanol report that whenever natural gas or mixtures of methane and ethane were used instead of pure methane the oxidation reaction was triggered at lower temperatures . Ito et al [2] found that an increase of the ethane concentration over a methane oxidative coupling catalyst ($Li^+$ / $MgO$) improved the ethylene production. Westbrook and Pitz [18] reported that traces of ethane and propane shorten the ignition time of methane mixtures with air.

We have further investigated the effect of the ethane on the methane conversion and selectivity by varying the amount of ethane in the feed . Figure 4 shows the % selectivity of the various products versus the % $CH_4$ conversion for silicic acid at the temperature range of 833 to 893 K. Conditions (1) and (2) correspond respectively to 0.14 mol % and 1.25 mol % of ethane in the feed stream (based on methane) . The increase in the ethane percentage in the feed enhances the ethylene, HCHO and $CO_2$ formation and suppresses the CO production. The most dramatic increase occurs in the ethylene selectivity and thus it would be very reasonable to attribute the ethylene formation almost exclusively to the ethane. The improvement in the formaldehyde selectivity could be due to the fact that the ethane and/or ethylene interactions with the surface inhibit the destruction of formaldehyde. At a conversion level of 5 % the increase of the ethane percentage in the feed from 0.14% to 1.25 % improves the selectivity of useful products (ethylene and formaldehyde) from 30% to 38%.

Runs of varying ethane concentration were performed over quartz tubes at 913 K and 445 kPa. The results obtained are shown on Figure 5. It is clear that the ethane in the feed has a very dramatic effect in the conversion of methane. By increasing the mol percent of ethane from 1.25% to 5.2 % based on methane, the conversion of methane nearly doubled from 1.8% to 3.2 % . The ethane conversion also increased from 10% to 40 % and always remained higher than the methane conversion. At the highest ethane mol percent of 8.9% complete conversion of ethane (90 % ) and a 34.4% conversion of methane occured. High conversions favored the CO and $CO_2$ formation, at the expense of formaldehyde and ethylene.

Ethylene is considered as a primary product of the ethane combustion formed via the oxidative dehydrogenation of the $C_2H_5$ · radicals, in an analogous way that formaldehyde is a primary product of the methane combustion formed from the oxidation of $CH_3$· radicals [14]. Therefore, the same silica surfaces that produce formaldehyde from methane can lead to the formation of ethylene from ethane. The conversion of ethane was always three to five times higher than the conversion of methane and this is in qualitative agreement with the experimental values of Bohme and Fehsenfeld [19] where it was reported that the probability for the first hydrogen abstraction increases with the size of the hydrocarbon chain. The ethane molecule apart from forming $C_2H_5$· radicals by hydrogen abstraction is also likely to act as a source of $CH_3$· radicals formed via C-C bond breakage. Experimental data show that the rate of formation of $CH_3$· radicals from ethane in this way is two orders of magnitude higher than the rate of formation of these radicals from methane [20]. Therefore the $C_2H_5$· , $CH_3$· as well as the H· radicals, which are generated from ethane easier than from methane could activate methane or
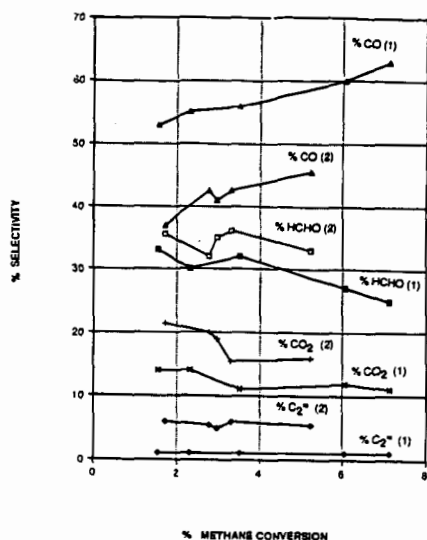
FIGURE 4 % Selectivity of the various products vs % CH$_4$ conversion over silicic acid in the temperature range of 833 to 893 K as a result of the variation of the ethane concentration in the feed. (1): 0.14 mol % ethane based on methane, flowrates 10% CH$_4$ in Ar 31 cm$^3$ STP /min, oxygen 3 cm$^3$ STP /min, at 380 kPa and over 535 mg of catalyst. (2) : 1.25 mol % ethane based on methane, flowrates 10% CH$_4$ in Ar 50 cm$^3$ STP /min, oxygen 5 cm$^3$ STP /min, at 360 kPa and over 504 mg of catalyst.
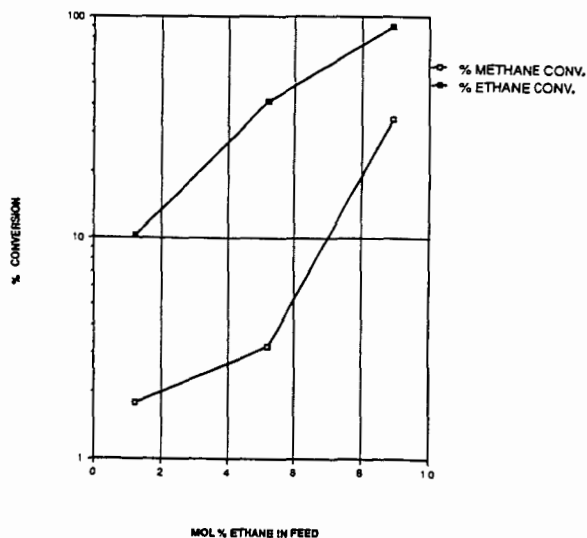


FIGURE 5 Methane and ethane conversions achieved over quartz glass at 913 K and 445 kPa as a function of the mol % ethane based on methane and ethane . Molar ratio of C to O$_2$ from 0.988 to 1.043.

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even interfere in the process of the chain propagation occuring during the methane oxidation-combustion.

## Methane oxidation over $MoO_3$ $WO_3$ and $H_3BO_3$ co-gels with Ludox silica

Ammonium heptamolybdate, ammonium metatungstate and $H_3BO_3$ were dissolved in Ludox colloidal silica. The pH was then adjusted either with nitric acid or with ammonium hydroxide and high surface area co-gels up to loadings of 12% by weight of $MoO_3$, $WO_3$ and $H_3BO_3$ on $SiO_2$ were prepared. Loadings of up to 5% by weight of $MoO_3$ led to complete oxidation of methane to $CO_2$ under an increased overall activity. Loadings of 5% by weight of $WO_3$ did not have any significant effect neither in the methane oxidation activity of the plain Ludox nor in the product distribution. A mechanical mixture of 5% by weight $MoO_3$ with Ludox exhibited almost identical activity and selectivity results as the 5% co-gel of $MoO_3$. This may suggest that at the high loadings used in the co-gels with Ludox $MoO_3$ may be present as a bulk phase.

As shown on Table 4 the boric acid co-gels dramatically improved the yields of formaldehyde over the plain silicas. It appears that while silica is responsible for the primary activation of methane, boron preserves the formaldehyde from further oxidation and / or decomposition to CO.

TABLE 4

Effect of boron in the activity and selectivity of Ludox silica at 903 K.

| Compound | %Overall conversion | % Selectivity | | | |
|---|---|---|---|---|---|
| | | HCHO | $C_2^=$ | CO | $CO_2$ |
| Ludox silica gel | 5.2 | 8 | 13 | 55 | 24 |
| 7% $H_3BO_3$ / Ludox silica co-gel | 4.9 | 47 | 12 | 34 | 7 |

Flowrates: 10% $CH_4$ in Ar=49.3 STP / min, $O_2$=5 $cm^3$ STP / min. P= 480 kPa. Ethane in feed: 1.25 mol% based on methane.

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